XV. "Researches on the Hydrocarbons of the series $C_n H_{2n+2}$.—No. V. On Octyl compounds." By C. Schorlemmer. Communicated by Prof. Stokes, Sec. R.S. Received June 17, 1869.

After I had found that the octylalcohol obtained by distilling castor oil with caustic soda, is methyl-hexyl carbinol, or a secondary alcohol*, it appeared to me of great interest to study the chemical structure of those alcohols which can be obtained from the different hydrocarbons of the formula $C_8 H_{18}$, the more so as Cahours and Pelouze assert that the derivatives of the octane contained in petroleum are identical with those derived from the castor-oil alcohol†, a statement which was afterwards confirmed by Chapman ‡.

The hydrocarbons which I used for my experiments were hydride of octyl, or octane from petroleum, and the hydrocarbon of the same composition, which I obtained by acting upon iso-octyl iodide with zinc and hydrochloric acid. The two hydrocarbons, as well as their derivatives, resemble each other in their physical properties so much, that one would be inclined to consider them as identical; their chemical properties, however, prove that they are only isomeric.

(1) *Derivatives of Octane from Petroleum.*

The boiling-point of this hydrocarbon is given differently by different observers between 116° and 120°; according to my latest researches, it appears to boil a few degrees higher. After fractionating it for a very long time, the greater portion was found to boil between 120° and 125°; it was now heated with nitric acid and again fractionated over sodium. A considerable portion distilled now at 119°–122°, but by far the largest quantity at 122°–125°. From this latter portion I prepared the octyl-chloride, a colourless liquid, which smells like oranges, and boils at 173°–176°. This chloride was heated up to 200° for several hours with concentrated acetic acid and potassium acetate. It was thus completely decomposed; the chief product of the reaction consisted of octylene, besides that a much smaller quantity of octyl-acetate had been formed. This ether is a colourless liquid, boiling at 200°–205°, and having a pleasant pear-like odour. It was converted into octyl-alcohol by heating it with an alcoholic solution of caustic potash. This alcohol, after being purified by washing it several times with water, and drying over fused potassium carbonate, was obtained as a colourless oily liquid, boiling at 180°–182°, and possessing exactly the odour of methyl-hexyl carbinol.

The alcohol was oxidized by mixing it slowly with a cold solution of 2 parts of potassium dichromate and 3 parts of sulphuric acid in 10 parts of water, care being taken to avoid as much as possible any elevation of

* Proc. Roy. Soc. vol. xvi. p. 376. † Ann. Chem. Phys. 4 ser. vol. i. p. 53.
‡ Journ. Chem. Soc. N. S. vol. iii. p. 296.

temperature during the reaction. As soon as a permanent brownish tinge showed that a slight excess of chromic acid was present, no more of the oxidising mixture was added. The liquid was shaken from time to time, and distilled after a few hours. The acid distillate was neutralized with sodium carbonate; only a small quantity of an acid was formed; the chief oxidation-product consisted of a neutral oil, having the odour of methyl-œuanthol, and, like this compound, it formed with hydrogen-sodium sulphite a crystalline compound. The liquid having no constant boiling-point, and the quantity being only small, I did not analyze it, but oxidised it further by heating it with the chromic-acid solution. The acid distillate was neutralized with sodium carbonate, the solution of the sodium salts was evaporated and distilled with diluted sulphuric acid. An oily acid, distilled over the residue in the retort, contained a large quantity of acetic acid, which was obtained pure by several distillations; from it silver acetate was prepared and analyzed.

0·3355 of this salt contained 0·2160 silver.

Calculated for $C_2H_3AgO_2$.	Found.
64·67 per cent. Ag.	64·38 per cent.

The distillate, which contained the oily acid, was neutralized with an excess of barium carbonate, boiled and filtered. On evaporation, the barium salt separated in form of an amorphous skin; it could not be obtained in the crystalline state; I therefore dissolved it again in more water, and precipitated it fractionally with silver nitrate.

1st Precipitate .. 0·1535 gave 0·0754 silver.
2nd „ .. 0·3718 „ 0·1798 „

Calculated for silver caproate, $C_6H_{11}AgO_2$.	Found. (1)	(2)
48·43 per cent. Ag.	49·12	48·36.

In the liquid, from which the second precipitate had been filtered off, a further addition of silver nitrate did not give any more precipitate. On evaporating it, small granular crystals separated, the analysis of which showed that they consisted of impure silver acetate; 0·5540 contained 0·3440 silver, or 63·23 per cent.

Besides caproic and acetic acids, a small quantity of an acid having the composition of caprylic acid was formed. This acid was precipitated probably as a basic salt, together with the excess of barium-carbonate, used in neutralizing the oily acid; it could not be extracted by boiling water. On dissolving the mixture of barium-salt in diluted nitric acid, oily drops separated. The liquid was distilled, the distillate neutralized with ammonia and precipitated with silver nitrate in two fractions,

1st Fraction .. 0·1344 contained 0·0566 silver.
2nd „ .. 0·0465 „ 0·0203 „

Calculated for $C_8H_{15}AgO_2$	Found. (1)	(2)
43·02 per cent. Ag.	42·11 per cent.	43·87 per cent.

(2) *Derivatives of Octane from Methyl-hexyl Carbinol.*

The alcohol obtained from castor oil is easily converted into its corresponding hydrocarbon by treating it first with iodine and phosphorus, and acting upon the iodide thus obtained with zinc and hydrochloric acid.

I have already described this hydrocarbon in a former communication; it boils constantly at 124° C. The octyl-chloride obtained from it has only a faint orange-like smell; it boils at 174°–176°. Heated with concentrated acetic acid and potassium-acetate to 200°, it is decomposed after a few hours, octyl-acetate and octylene being formed in about equal quantities, whilst the chloride obtained from petroleum gave about three times more octylene than acetate.

This acetate boils at 198°–202°, and has the same pear-like odour as that described above. The alcohol prepared from it by heating it with an alcoholic solution of caustic potash, had no constant boiling-point; it distilled between 180° and 190°; the greatest portion between 182° and 186°; its odour is very much like that of methyl-hexyl carbinol. As I had only about 4 grammes, I could not subject it to fractional distillation. On oxidizing it with the chromic-acid solution, the greatest care was taken to avoid rise of temperature, the solution being added very slowly until a permanent brownish colour showed that a slight excess of chromic acid was present, the vessel being all the time surrounded by cold water. In order to have as decisive results as possible, I oxidised at the same time, and under exactly the same circumstances, 4 grammes of methyl-hexyl carbinol. The liquids were allowed to remain together for a day, and were frequently shaken, then distilled, and the distillate neutralized with sodium carbonate.

The two results differed very widely; methyl-hexyl carbinol was, as in my former experiments, converted into methyl-œnanthol, a small portion of which was oxidised further to acetic and caproic acids. The caproic acid was separated by repeated distillation from the acetic acid, and neutralized with ammonia. From this solution I purposed to prepare silver salts by fractional precipitation, but only one precipitate was obtained.

0·1113 of this salt contained 0·0536 silver.

Calculated for $C_6H_{11}AgO_2$.	Found.
48·43 per cent. Ag.	48·16 per cent. Ag.

The octylalcohol from the pure hydrocarbon yielded a large quantity of an oily acid, and a smaller portion of a neutral oil, but not a trace of acetic acid. The oily acid has the composition of caprylic acid; it was analyzed as the silver salt, which was obtained by fractional precipitations.

1st Precipitate .. 0·3500 contained 0·1700 silver.
2nd ,, .. 0·3090 ,, 0·1335 ,,

Calculated for $C_8H_{15}AgO_2$.	Found. I.	Found. II.
43·02 per cent.	42·86 per cent.	43·20 per cent.

The neutral oil had quite the properties of an acetone; it gave a crystalline compound with hydrogen-sodium sulphite, and was not changed any further by the oxidising mixture in the cold; but on heating them together, oxidation took place and fatty acids were formed, which appeared to be a mixture of propionic and valerianic acids; of acetic acid not a trace could be detected.

1st	Fraction of the silver salt	.. 0·1325	gave 0·0675 silver.
2nd	,, ,, ,,	.. 0·2732	,, 0·1385 ,,
3rd	,, ,, ,,	.. 0·1562	,, 0·0780 ,,

Calculated for Silver valerate.	Calculated for Silver caproate.	Found. I.	Found. II.	Found. III.
51·67 per cent. Ag.	48·43 per cent. Ag.	50·94	50·69	50·0

The percentage amount of silver contained in these salts corresponds better with that of valerate than that of caproate; most probably a little caprylic acid was still present, which caused the amount of silver to be a little too small.

The solution from which these silver salts had been precipitated gave on evaporation small granular crystals, having the composition of silver propionate.

0·1738 gave 0·1033 silver.

Calculated for $C_3H_5AgO_2$.	Found.
59·67 per cent. Ag.	59·43. per cent.

From the results of my experiments I draw the following conclusions:—

(1) The octyl alcohol, obtained from the hydrocarbon C_8H_{18}, occurring in American petroleum, consists chiefly of methyl-hexyl carbinol, $\left.\begin{matrix}CH_3\\C_6H_{13}\end{matrix}\right\}CH\,OH$, and is therefore identical with the alcohol obtained from castor oil. Not only the physical properties of the two and their derivatives agree*, but also their oxidation products are the same; they both give methyl œnanthol or methyl-hexyl acetone, $\left.\begin{matrix}CH_3\\C_6H_{13}\end{matrix}\right\}CO$, which, by further oxidation, splits up into acetic and caproic acids.

Besides this secondary alcohol, there is also formed a smaller quantity of a primary alcohol, as amongst the products of oxidation an acid containing eight atoms of carbon was found.

(2) The hydrocarbon, C_8H_{18}, which is formed by replacing in methyl-hexyl carbinol the group hydroxyl HO by hydrogen, is different from that

* The only exception is the boiling-point of the acetate, which I found to be 200°–205°, whilst that from castor oil boils, according to Bouis, at 193°.

found in petroleum. It gives, by the proper reactions, a considerable quantity of a primary alcohol, and a smaller quantity of a secondary one; the latter is not identical with methyl-hexyl carbinol, but consists most probably of ethyl-amyl carbinol, $\left.\begin{matrix} C_2 H_5 \\ C_5 H_{11} \end{matrix}\right\}$ CH OH, as, on oxidation, it yields valerianic and propionic acids.

The primary alcohol appears to differ from the primary octyl alcohol, which has been found lately by Zincke in the seeds of *Heracleum spondylium**. The essential oil of these seeds consists chiefly of an octyl acetate, boiling at 206°–208°, and possessing an orange-like smell, whilst that which I obtained smells strongly of pears, and boils at 198°–202°. By oxydising his alcohol, Zincke obtained a caprylic acid, which solidified at 12°, whilst the acid which I got remained liquid at 0°. Zincke's alcohol is most likely the normal alcohol, and that which I obtained an alcohol containing the group isopropyl†.

(3) On acting upon the hydrocarbons of the series $C_n H_{2n+2}$ with chlorine, a mixture of primary and secondary chlorides is formed. This is proved by the fact that the alcohols derived from these chlorides yield, on oxidation, besides an acid containing the same number of atoms of carbon as the alcohol, also acetones, or the characteristic oxidation products of secondary alcohols. Not only the above researches show this, but also my former experiments on the oxidation of amyl-alcohol prepared from the hydride, which gave, besides valerianic acid, also acetic acid and the acetone, $C_5 H_{10} O$‡.

It is certainly very remarkable that the hydrocarbon from petroleum yields *methyl-hexyl carbinol*, whilst the hydrocarbon which is obtained from methyl-hexyl carbinol is not reconverted into this alcohol, but gives *ethyl-amyl carbinol*, and besides a primary alcohol.

The further investigation of this subject is certainly of the highest theoretical interest; but there is great difficulty in pursuing this research, as I have already observed, in consequence of the small yield of pure alcohol from large quantities of the hydrocarbons.

XVI. "On the Derivatives of Propane." By C. Schorlemmer. Communicated by Prof. Stokes, Sec. R.S. Received June 17, 1869.

The chief product obtained by the action of chlorine upon propane consists, as I have already stated in my last communication §, of propylene dichloride; besides this compound, we find in smaller quantities the normal propyl chloride and products richer in chlorine, which boil between

* Zeitschrift für Chemie, N. F. vol. v. p. 55.

† Proc. Roy. Soc. vol. xvi. p. 379.

‡ Ibid. p. 374.

§ Ibid. No. 111, 1869.